Intermolecular and Intramolecular Hydrogen Bonding of Poly(dimethylsiloxane)urethane-Graft–Poly(methyl methacrylate) Copolymers Based on 2,4-TDI and *m*-XDI

Chen-Chi M. Ma,[1] Feng-Yih Wang,[2] Yi-Chang Du,[1] Chen-Li Wu,[1] Chin-Lung Chiang,[1,3] Albert Y. C. Hung[4]

[1]*Department of Chemical Engineering, National Tsing-Hua University, Hsin-Chu, Taiwan, 30043, People's Republic of China*
[2]*PM Technical of Photoresist Division, Eternal Chemistry Company, Kaohsiung Country, Taiwan, 831, People's Republic of China*
[3]*Department of Industrial Safety and Health, Hung-Kuang Institute of Technology, Sha-Lu, Taiwan, 433, People's Republic of China*
[4]*Department of Food Nutrition, Chung Hwa Medical Technology, Tainan Hasien, Taiwan, 71741, People's Republic of China*

ABSTRACT: In this study, poly(dimethylsiloxane)urethane–graft–poly(methyl methacrylate) (PDMS urethane–g–PMMA) copolymers with low crosslinking density were synthesized. Glass transition temperatures of the copolymers were investigated by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Results confirm that PDMS urethane–g–PMMA is miscible in the 2,4-TDI (2,4- toluene diisocyanate) system, whereas it is partially miscible in the *m*-XDI (*m*-xylene diisocyanate) system. Free, intra- (urethane–urethane), and inter- (urethane–ester) association hydrogen bonding exist in the urethane group of copolymers. The inter-association hydrogen bonding can improve the compatibility of the copolymer components. The relationship between the frequency shift and enthalpy confirm the distribution of hydrogen bonding in the macromonomer and copolymer. Ninety percent of the hydrogen bonding is by interassociation in the 2,4-TDI system. The intra-association hydrogen bonding in the *m*-XDI system is higher than that in the 2,4-TDI system. Consequently, aggregation may occur easily in the siloxane-grafted chain in the *m*-XDI system. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 962–972, 2002

Key words: copolymerization; polyurethanes; association; glass transition; macromonomers

INTRODUCTION

Poly(methyl methacrylate) (PMMA), prepared by free radical polymerization, exhibits high transparency, weather resistance, and nontoxicity. Furthermore, it is easy to process in a mold. However, low impact strength, low initial temperature of thermal decomposition, and poor abrasion resistance limit its applications.

Poly(dimethylsiloxane) (PDMS) possesses many unique properties, such as low glass transition temperature (T_g), high flexibility, good thermal stability, and low surface energy. PDMS can be used to improve PMMA by physically blending or by chemical techniques.[1–8] The objective of this study is to focus on the PDMS–g–PMMA system. The solubility parameter of PDMS [15.34 $(J/cm^3)^{1/2}$] is different from that of PMMA [18.6 $(J/cm^3)^{1/2}$]. Thus, if PDMS–g–PMMA does not contain any other functional groups, which could improve the compatibility of PDMS and PMMA, the copolymer will show phase separation.[7] The interassociation hydrogen bonding is a stronger intermolecular force than van der Waals force, thus it can improve the compatibility of two different structural polymers.[9,10] It has been reported that the structural difference in the diisocyanates may affect the properties of urethane-contained polymer.[11]

For this study, 2,4-toluene diisocyanate (2,4-TDI) and *m*-xylene diisocyanate *(m*-XDI) were selected to synthesize two different types of PDMS urethane–g–PMMA copolymers. Several methods are suggested to prepare graft copolymer of PDMS with PMMA.[4–8] The macromonomer technique was utilized by us to synthesize graft copolymers because it possesses several unique advantages. For instance, the number and chain length of the graft branches can be easily controlled by the macromonomer method. PDMS urethane–g–PMMA copolymers were prepared by the macromonomer technique in this study.

Correspondence to: C-C. M. Ma (ccma@che.nthu.edu.tw).

TABLE I
Materials Used in the Study

No.	Reagent	Structure and properties	Supplier
1	α, ω-bis-(Hydroxypropyl) polydimethyl siloxane (X-22-160AS) PDMS-diol	$CH_2 \quad CH_3$ | \quad | $HOCH_2CH_2CH_2$—$(SiO)n$—Si—$CH_2CH_2Ch_2OH$ | \quad | $CH_3 \quad CH_3$ EW = 518.5,	Shin Etsu Company (Japan)
2	m-Xylene diisocyanate (m-XDI)	CH_2—$N=C=O$ CH_2—N—C—O FW = 188.18, purity > 99%	Tokyo Chemical Company (Japan)
3	2,4-Toluene diisocyanate (2,4-TDI)	CH_3 $N=C=O$ $N=C=O$ FW = 174.16, purity > 99%	Tokyo Chemical Company (Japan)
4	2,2′-Azobis-isobuty ronitrile (AIBN)	FW = 164.21, purity = 99%	Sho Wa Chemical Company (Japan)
5	Methyl methacrylate (MMA)	FW = 100.12, purity = 99%	Lancaster Company (England)
6	2-Hydroxyethyl methacrylate (HEMA)	FW = 130.14, purity = 96%	Fisher Sci. Company (Belgium)
7	Methyl alcohol	CH_3OH FW = 32.04, anhydrous, purity = 99.8%	Fisher Sci. Company (Belgium)
8	Tetrahydrofuran (THF)	FW = 72.11, HPLC/Spestro	Tedia Company (Fairfield, OH)

2,4-TDI and m-XDI were selected to synthesize two copolymer systems. The compatibility and interassociation hydrogen bonding of PDMS urethane–g–PMMA copolymers, caused by different structures of 2,4-TDI and m-XDI, will be discussed.

EXPERIMENTAL

Materials

The materials that were used in this study are summarized in Table I. PDMS-diol was dried under vacuum at 60°C for 6 h. The methyl methacrylate (MMA) and 2 hydrooxyethyl methacrylate (HEMA) were purified by vacuum distillation in this study.

Synthesis of macromonomers[12]

Two types of PDMS–urethane–methacrylate macromonomers based on 2,4-TDI and m-XDI were synthesized by adding 2 mol of PDMS-diol with 0.15 wt % stannous octoate into benzene solutions containing 10 wt % m-XDI or 2,4-TDI and stirring at 60°C in a dry atmosphere. When the absorption peak of the hydroxyl group in the infrared (IR) spectra disappeared, equimolar amounts of methanol and HEMA containing 1 wt % hydroquinone were added to the mixture and the temperature was kept at <60°C to prevent thermal polymerization. When the absorption peak of

the isocyanate group at 2270 cm^{-1} in the IR spectra was absent, the reaction was completed. The contaminants were removed from the reaction mixture by decolorizing carbon, and solvent was evaporated by vacuum distillation.

In this study, the macromonomer based on 2,4-TDI and hydroxyl-containing reactants is referred to as PRETDI, and the macromonomer originating from m-XDI is called by PREXDI.

Synthesis of PDMS urethane–g–PMMA[12]

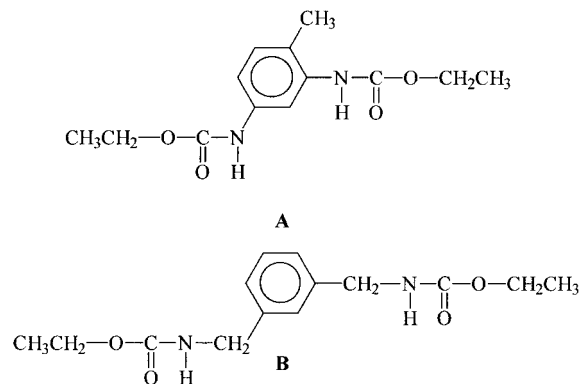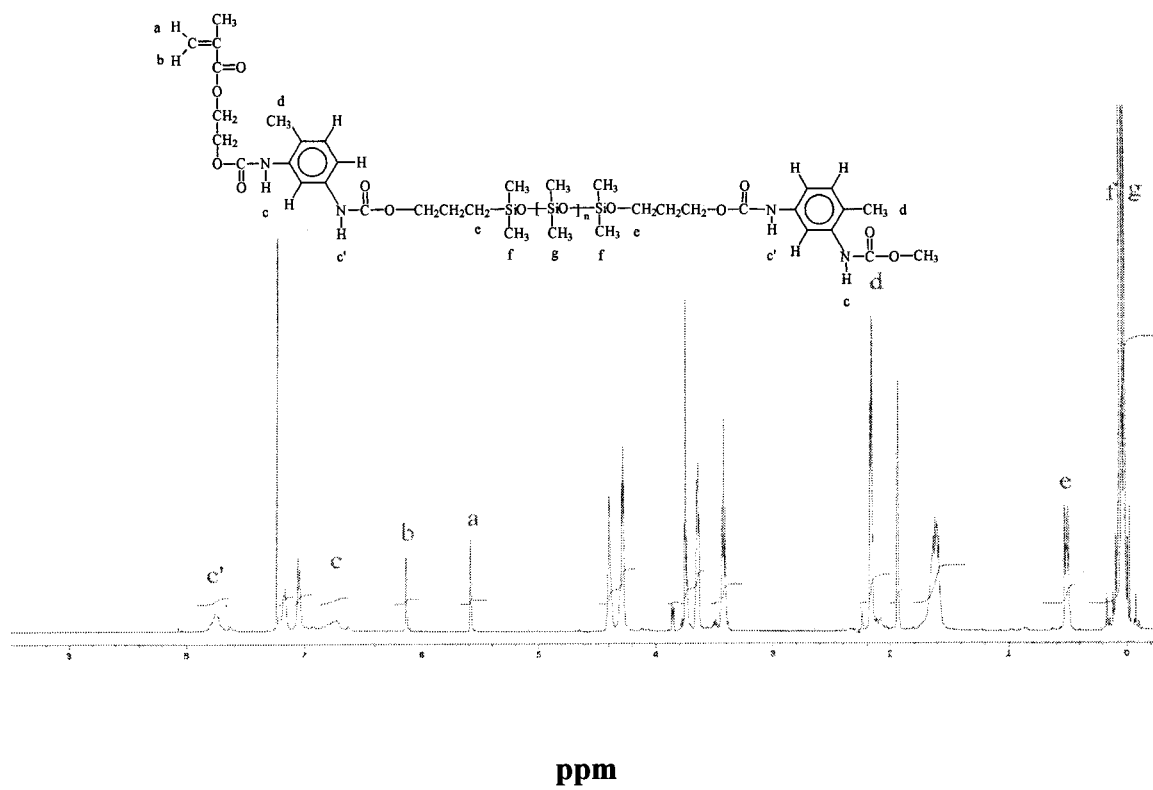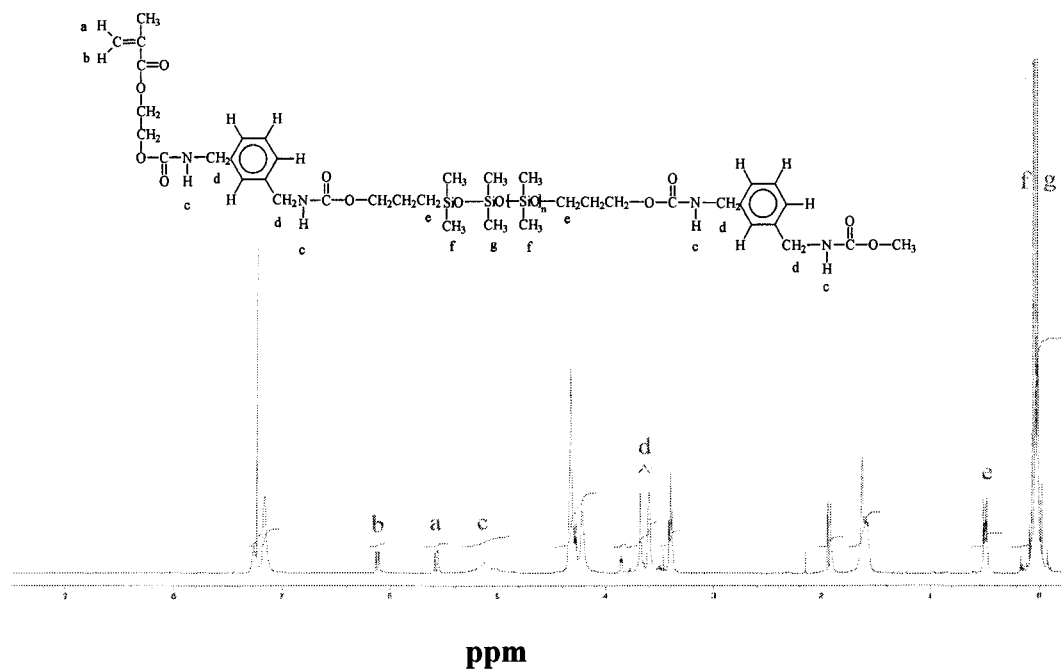Various amounts of PDMS–urethane macromonomers and MMA monomers were mixed and copoly-

Figure 1 Molecular structures of (A) TBEU and (B) XBEU.

Figure 2   ¹H NMR spectra of (A) PRETDI and (B) PREXDI.

TABLE II
Swelling Ratios of Copolymers and Molecular Weights of PRETDI and PREXDI

Parameter	PRETDI		PREXDI	
	GPC	NMR	GPC	NMR
M_n	1593	1602 (1547)[a]	1776	1687 (1575)[a]
M_w	1768	—	2300	—
PDI	1.469	—	1.295	—

[a] Theoretical value in parentheses.

merized by adding 0.3 wt % 2,2'-azobis-isobutyronitrile (AIBN) at 60°C in a nitrogen atmosphere. As the viscosity of the reaction mixture was raised rapidly, it was cooled down to room temperature and then was transferred to a mold that consists of two sheets of glass. The copolymerization proceeded again at 60°C for 12 h and 90°C for 3 h. The reaction was completed when the absorption peak of carbon=carbon at 1650 cm^{-1} in the IR spectra disappeared. A pure PMMA specimen was synthesized by the same method without macromonomers.

In this study, the symbols SiTY and SiXY are used to represent the copolymers, where Si is the siloxane-polyol (i.e., PDMS-diol), T is 2,4-TDI, X is *m*-XDI, and Y is the content of diisocyanate in each unit (i.e., phr = part per hundred parts of copolymer), which was used to indicate the content of copolymer. For instance, SiT22.5 represents the copolymers based on 22.5 phr 2,4-TDI macromolecules.

Model compounds for synthesizing PDMS urethane–g–PMMA

Two types of model compounds based on 2,4-TDI and *m*-XDI, respectively, are synthesized by adding 2 mol of ethanol with 0.15 wt % stannous octoate into benzene solution containing 10 wt % *m*-XDI or 2,4-TDI with stirring at 60°C in a dry atmosphere. When the absorption peak of the isocyanate group at 2270 cm^{-1} in the IR spectra disappeared, the reaction was completed.

The model compound 2,4-toluene-bis(ethylene urethane) is a reaction adduct of 2,4-TDI with ethanol and is represented by TBEU; on the other hand, the model compound *m*-xylene-bis(ethylene urethane) is an adduct of *m*-XDI with ethanol and is represented as XBEU (see Figure 1).

TABLE III
Swelling Ratios of Copolymers

| Parameter	SiT3.75	SiT22.5	SiX3.75	SiX22.5
Swelling ratio	4.16	3.27	5.88	3.72
Soluble fraction (wt %)	1.74	1.21	1.89	1.42
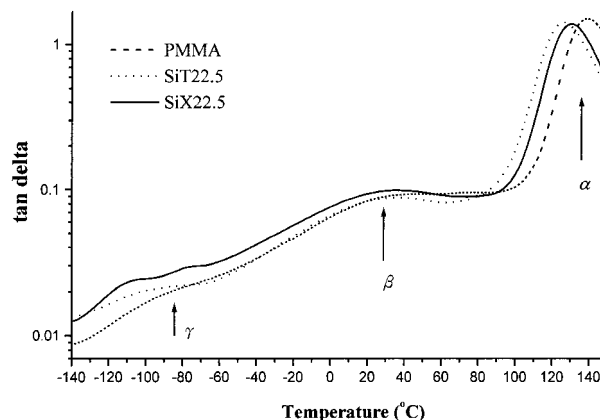
Figure 3 Tan δ curves of PMMA, SiX22.5, and SiT22.5.

Characterization

The structures of PRETDI and PREXDI were characterized by IR spectroscopy, gel permeation chromatography (GPC), and nuclear magnetic resonance spectroscopy (NMR). The characteristic absorption peaks of macromonomers in IR and NMR spectra were detected with a Perkin Elmer IR-842 IR spectrometer and a Bruker AM 400 MHz ^{1}H NMR spectrometer, respectively. The chemical shift (δ) of NMR spectra is given in ppm, and CDCl$_3$ was the solvent. The molecular distribution of macromonomers was measured with a Waters 510 GPC equipped with an refractive index detector. Tetrahydrofuran (THF) was used as mobile phase at a flow rate of 1 mL/min at 40°C.

The IR spectra were detected on a Fourier transform infrared (FT-IR) spectrometer (Bio-Rad FTS-155, Hercules, CA). In all cases, at least 16 scans with an accuracy of 2 cm^{-1} were signal-averaged. For liquid samples, an adequate permanently sealed cell with NaCl windows and 0.05-mm thickness (Wilmad, Buena, NJ) was used. A single optical path was used to study the interassociation between ethyl acetate and
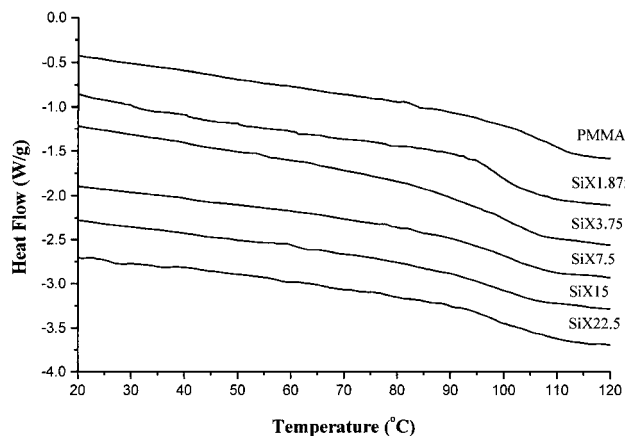
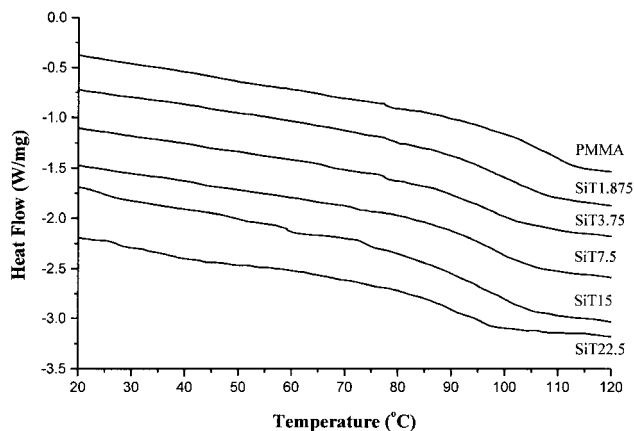**Figure 4** DSC curves of copolymers in the 2,4-TDI system.

Figure 5 DSC curves of copolymers in the *m*-XDI system.

Figure 7 Possible hydrogen bonding in this study: (A) intramolecular hydrogen bonding between urethane groups; (B) intermolecular hydrogen bonding between -NH and ester group in PMMA.

TBEU or XBEU. The Beer–Lambert law was obeyed on all model compound solutions in the absorption range. Chloroform was used as solvent in this study because it is nonpolar.[8, 9]

The T_g values of the PDMS urethane–g–PMMA were measured with a differential scanning calorimeter (DSC; Du-Pont, DSC model 2900). The heating rate was 10°C/min within a temperature range 20–120°C. The measurements were made with 3–4 mg of sample on a DSC plate after the specimens were quickly cooled to room temperature following the first scan. The T_g values were determined at the midpoint of the transition point of the heat capacity (C_P) changed, and the reproducibility of T_g values was estimated to be within ±2°C.

The damping factor (tan δ) of polymer was measured as a function of temperature at 1Hz with a dynamic mechanical analyzer (DMA; TA DMA 2980) at a heating rate of 3°C/min. The T_gs of the copolymers were detected with a DSC (TA DSC 10) at a heating rate of 10°C in N_2 atmosphere.

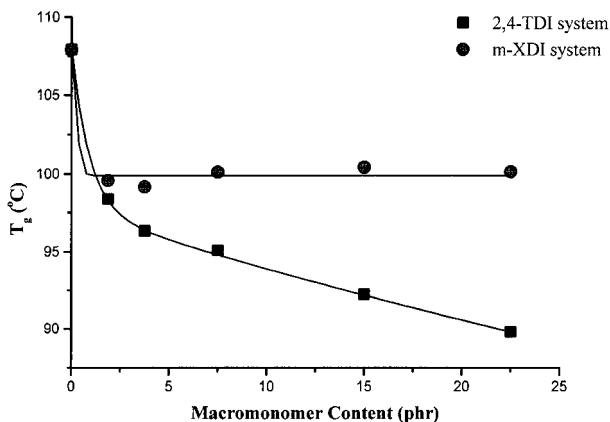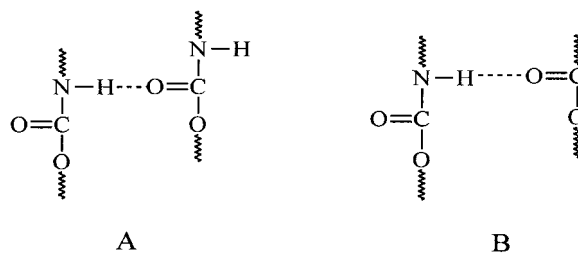The abrasion resistance was tested according to ASTM D4060, with the following testing conditions:

Figure 6 Relationship between T_g and macromonomer content in the copolymers.

an emery wheel (CS-17); load set at 1 kg; rotation rate of 60 rpm.

RESULTS AND DISCUSSION

Characterization

The ^{1}H NMR spectra of PRETDI and PREXDI are shown in Figures 2a and 2b, respectively. The protons of vinyl groups shift to both 5.58 and 6.13 ppm. The hydrogen in the urethane group of PREXDI shifts to 5.12 ppm. On the other hand, the hydrogen of urethane group of PRETDI possesses chemical shifts of 6.73 and 7.76 ppm. The number-average molecular weights (M_n) of PREXDI and PRETDI, measured by GPC and NMR, are listed in Table II. A good correspondence between theoretical values and NMR results was obtained. The polydispersity indices (PDI; i.e., molecular weight distribution) of PREXDI and PRETDI are also listed in Table II.

Although the reactants are stoichiometric, reactivity parameters and reaction conversion may limit the chemical homogeneity of macromonomers. Chemical heterogeneity leads to few macromonomers that contain more or less than one vinyl group in the synthesized products. Copolymers synthesized by copolymerizing such macromonomers with MMA monomers are crosslinked slightly and contain a few macromonomers that have no reactivity. A swelling measurement was used to investigate the degree of crosslinking polymer. The soluble fraction of copolymer specimens, including nonreactive macromonomers and nonnetwork polymers, were determined by Soxhlet extraction using THF as solvent at the boiling point of THF for 3 days. The crosslinking densities of copolymers were obtained by determining the difference in volume of the specimens before and after the specimens were swelling with THF at room temperature for 1 week.[12]

The content of the soluble ratio and fraction of copolymers in the two systems are listed in Table III. The results indicate that those copolymers contain <2 wt % soluble species. PDMS urethane–g–PMMA copoly-

mers with low crosslinking density were synthesized in this study.

Compatibility of PDMS-urethane and PMMA segments of copolymers in *m*-XDI and 2,4-TDI systems

The loss tangent (tan δ) spectra of PMMA homopolymer and SiT22.5 and SiX22.5 copolymers, detected by DMA, are shown in Figure 3. The tan δ peak is associated with the partial loosening of the polymer structure because the functional groups and the small chain segments in the polymer can be moved easily. Tan δ curves of PMMA in Figure 3 show α relaxation (i.e., the onset of long-range, coordinated molecular motion) at 137°C. Furthermore, the β and γ relaxations (i.e., the rotation of ester side group and the rotation of the α-methyl group, respectively) are shown at 50 and −100°C, respectively.

The tan δ curve of SiX22.5 in Figure 3 shows that these relaxations of PMMA and PDMS segments occur at 131 and −110°C, respectively, indicating PDMS urethane and PMMA segments in the *m*-XDI system are partially miscible. The α and β relaxations of PMMA segments in SiX22.5 shift to lower temperature compared with the PMMA homopolymer. Furthermore, a peak is distinct at −74°C in the tan δ curve of SiX22.5. A similar result was also found in PMMA–g–PDMS, as reported by Smith et al.[7] These authors proposed that the degree of mixing might extend beyond the interface region between PMMA and PDMS microdomains.

The tan δ curve of SiT22.5 in Figure 3 shows that PDMS-urethane and PMMA segments are mixed well, because the α relaxation of PMMA segments in SiT22.5 is present at 126°C, close to that of SiX22.5. On the other hand, the α relaxation of PDMS segments in SiT22.5 is insignificant, a broad transition is observed at −90°C. This result implies that the miscibility of the copolymer in the 2,4-TDI system is better than that in the *m*-XDI system.

The relationship between PDMS-urethane content and the T_g of PMMA segments in two copolymer systems measured by DSC are shown in Figures 4–6. Low-temperature transitions of PDMS cannot be identified by the DSC curve. The T_gs of copolymers in the *m*-XDI system are independent of the macromonomer content, although the T_gs are all lower than those of PMMA homopolymers. On the other hand, the T_gs of PMMA segments of copolymers decrease with the macromonomer content, indicating that good miscibility existed in the 2,4-TDI system.

The miscibility of PDMS-urethane and PMMA segments of copolymers in 2,4-TDI and *m*-XDI systems was confirmed by DMA and DSC data. The structure of functional groups joined with urethane groups affects the strength of hydrogen bonding between

PMMA and urethane group and controls the miscibility of PDMS-urethane and PMMA segments, which will be discussed later.

Apparent integrated molar absorption coefficient in model compound based on 2,4-TDI and *m*-XDI

Intermolecular hydrogen bonding affects the miscibility of differential segments in copolymer. Therefore, the difference of enthalpy and the content of hydrogen
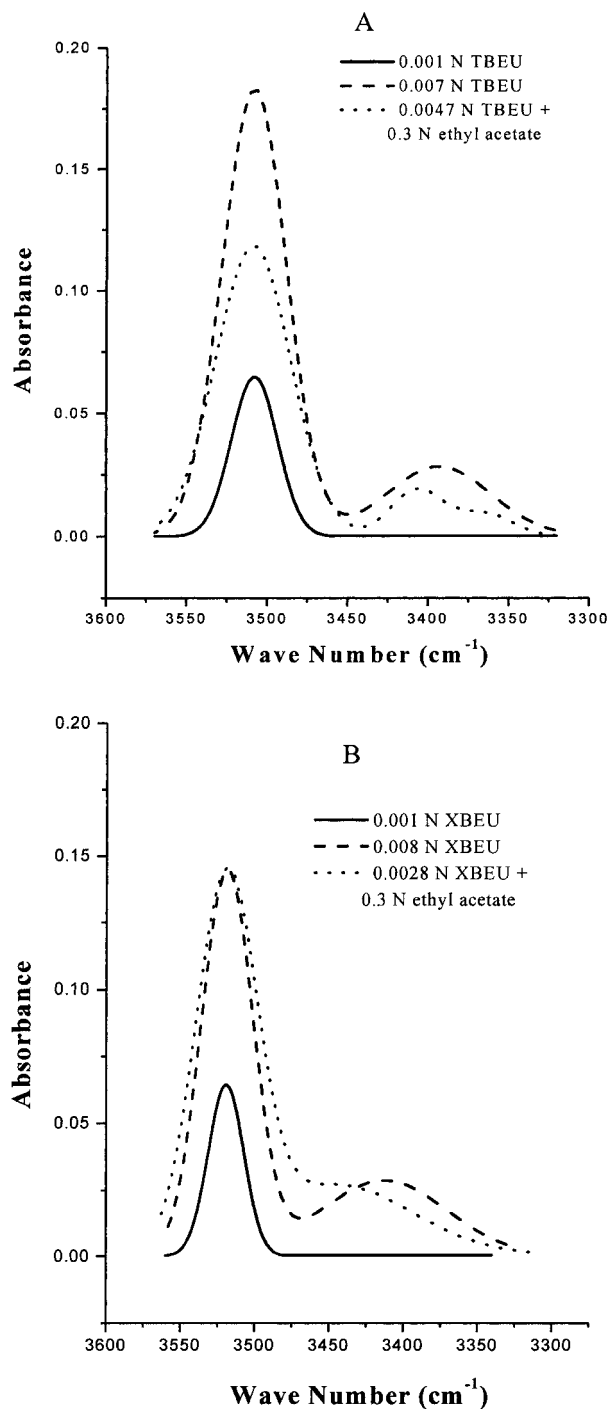

Figure 8   IR spectra of (A) TBEU and (B) XBEU in CCl₄.

TABLE IV
Apparent Integrated Molar Absorption Coefficients of TBEU and XBEU

Polymer system/molar absorption coefficient	"H free"—NH	—NH H-bonded to ethyl acetate —C=O	—NH H-bonded to urethane —C=O
0.001 N TBEU	2.339	—	—
0.007 N TBEU	9.120	—	2.317
0.0047 N TBEU + 0.3 N ethyl acetate	6.932	0.914	0.301
Apparent integrated molar absorption coefficient	2339	646	686
0.001 N XBEU	1.974	—	—
0.008 N XBEU	6.254	—	3.076
0.0028 N XBEU + 0.3 N ethyl acetate	2.103	1.002	0.055
Apparent integrated molar absorption coefficient	1974	637	607

TBEU: toluene-2,4-bis(ethyl urethane)
XBEU: xylene-m-bis(ethyl urethane)

bonding in PDMS urethane–g–PMMAs based on 2,4-TDI and m-XDI affects the miscibility. The relationship between the frequency shift and enthalpy can describe the intermolecular hydrogen bonding of these copolymers.[13–19] Two types of hydrogen bonding exist in PDMS urethane–g–PMMAs; these are intramolecular and intermolecular hydrogen bonding, as shown in Figure 7. Intramolecular hydrogen bonding is from urethane groups in grafted chain that react with urethane groups. Intermolecular hydrogen bonding is from urethane groups in grafted chain reacting with ester groups in the main chain of the copolymer.

The IR spectra of toluene-2,4-bis(ethyl urethane) (TBEU), xylene-m-bis(ethyl urethane) (XBEU), and ethyl acetate in chloroform at various concentrations are shown in Figure 8. As shown in Figure 8A, the peak at 3505 cm^{-1} is the free-urethane group for 0.001 N TBEU,[21] and the other peak at 3392.6 cm^{-1} is the hydrogen bonding of urethane group (intra-association hydrogen bonding) in 0.007 N TBEU. The peak at 3405 cm^{-1} is the hydrogen-bonded urethane group (interassociation hydrogen bonding) in 0.0047 N TBEU and 0.3 N ethyl acetate. As shown in Figure 8B, the peak at 3517 cm^{-1} is the free-urethane group for 0.01 N XBEU and the other peak at 3413.5 cm^{-1} is hydrogen-bonded urethane group (intra-association hydrogen bonding) in 0.008N TBEU. The peak at 3441 cm^{-1} is the hydrogen-bonded urethane group (inter-

association hydrogen bonding) in 0.0028 N TBEU and 0.3 N ethyl acetate.

The repeat unit of PMMA is almost the same as that of ethyl acetate because ethyl acetate has the same ester group. Hence, ethyl acetate was used as the model compound of PMMA. The apparent integrated molar absorption coefficients of free, intra-association hydrogen bonding and interassociation hydrogen bonding of the urethane group were calculated by the Beer–Lambert law, as shown in eq. 1,[21] and the results are summarized in Table III.

$$A = \int \log(T_o/T)\mathrm{d}\nu = \xi lc \qquad (1)$$

where A is the area of absorption peak (cm^{-1}), ν is the wave number (cm^{-1}), ξ is the apparent integrated molar absorption coefficient (1/mol-cm^2), the length of the path (l) is 1 cm, and c is concentration (N, equivalent mole).

The ratios of apparent integrated molar absorption coefficient of free, intra-association hydrogen bonding and interassociation hydrogen bonding of the urethane group were 3:1:1 in TBEU and XBEU systems, as shown in Table IV. However, the apparent integrated molar absorption coefficient was used to calculate the fraction of interassociation hydrogen bonding in the copolymers later.

TABLE V
Relationship between IR Frequency Shift and Enthalpy of Model Compounds

| Proton acceptor	Toluene-2,4-bis(ethyl urethane) $\Delta\nu$ (cm^{-1})	ΔH (kcal/mol)	Xylene-m-bis(ethyl urethane) $\Delta\nu$ (cm^{-1})	ΔH (kcal/mol)
Ethyl acetate	100	−3.29	76	−2.50
Diethyl ether	145	−3.45	123	−2.93
THF	175	−3.95	140	−4.06
Pyridine	275	−4.79	225	−4.06
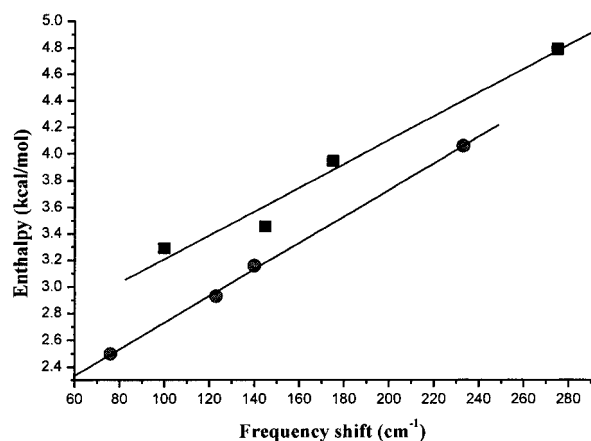
Figure 9 Correlation between the frequency shifts and enthalpy of TBEU (■) and XBEU (●) in their mixtures with various bases.

The relationship between the linear frequency shifts and the enthalpies of TBEU and XBEU systems

Enthalpies of the intra-association reaction of XBEU and TBEU were estimated from the observed shifts of the associated urethane bands, with the support of a correlation between band shifts and enthalpies.[20] The interassociation reactions between ethyl acetate and XBEU, and ethyl acetate and TBEU, were investigated by taking the IR spectra of the different proton acceptors, XBEU and TBEU, in chloroform solutions. Enthalpies of the self-association reaction of proton acceptor, XBEU and TBEU, were estimated from the observed shifts of the associated urethane bands, from the correlation between band shifts and enthalpies.[20] The relationship between frequency and the enthalpy of model compound is listed in Table V.

The correlation between enthalpy (ΔH) and frequency shifts ($\Delta \nu$) for the urethane band is illustrated in Figure 9. A linear relationship between frequency and enthalpy is also shown in Figure 9. The linear relationships between frequency shifts and enthalpies
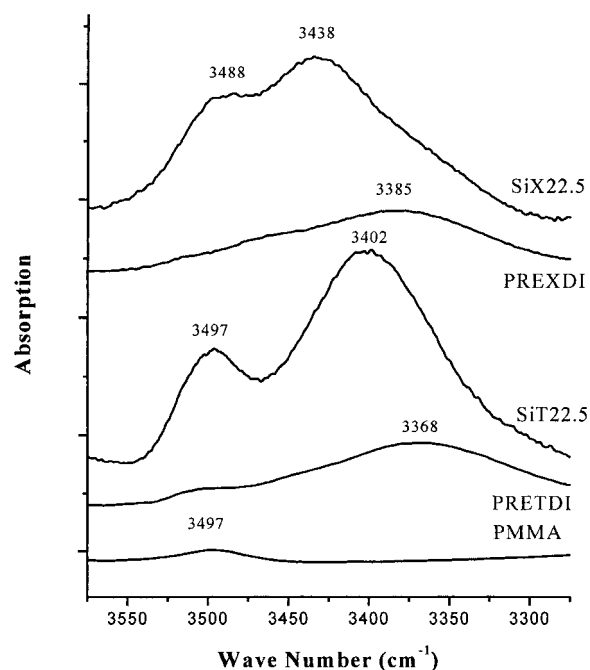
Figure 10 IR spectra of PMMA, macromonomers, and copolymers in 2,4-TDI and *m*-XDI systems.

for the 2,4-TDI and *m*-XDI systems are shown in eqs. 2 and 3, respectively:

$$-\Delta H = 8.96 \times 10^{-3} \Delta \nu + 2.312 \quad \text{(kcal/mol)} \quad (2)$$

$$-\Delta H = 10.55 \times 10^{-3} \Delta \nu + 1.672 \quad \text{(kcal/mol)} \quad (3)$$

Enthalpies of hydrogen bond formation of in XBEU and TBEU macromonomers are listed in Table VI. In the XBEU and TBEU systems, the interassociation enthalpy is higher than the intra-association enthalpy. The interassociation hydrogen bonding is the major hydrogen force in the macromonomers.

TABLE VI
Enthalpies of Hydrogen Bond Formation of XBEU and TBEU Macromonomers

Group	XBEU system		TBEU system	
	Peak (cm^{-1})	Enthalpy (kcal/mol)	Peak (cm^{-1})	Enthalpy (kcal/mol)
Overtone of carbonyl group	3497	—	3497	—
H "free"—NH	3517	—	3505	—
—NH H-bonded to urethane C=O	3413	−2.76	3392	−3.32
—NH H-bonded to ethyl acetate C=O	3441	−2.47	3405	−3.21

Figure 11 Structures of macromonomers.

Figure 13 Curve-fitting result of IR spectra of SiX22.5.
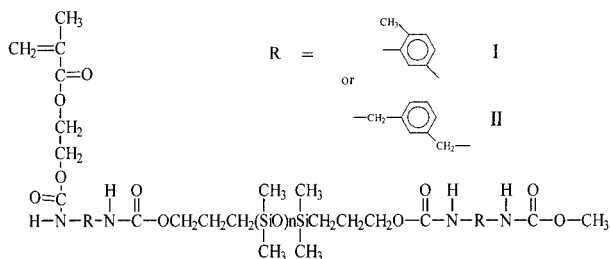
Hydrogen bonding contents of copolymers based on 2,4-TDI and *m*-XDI

IR spectra of PMMA, macromonomers, and copolymers in 2,4-TDI and *m*-XDI systems are shown in Figure 10. There is free, intra-, and inter-association hydrogen bonding in urethane groups of copolymers. The structure of the macromonomers containing urethane and ester groups is shown in Figure 11. The content of ester group of copolymer (MMA + macromonomer) is much higher than that of the macromonomer. However, the urethane absorption band in macromonomer is lower than that of the copolymers in *m*-XDI and TDI systems, as shown in Figure 10. Therefore, the intra-association hydrogen bonding is the major hydrogen bonding in copolymer, whereas the interassociation hydrogen bonding is the major hydrogen bonding in the macromonomer. There is an ester absorption band at 3497 cm^{-1}.

IR spectra of SiT22.5 and SiX22.5 are shown in Figures 12 and 13. There are four bands located within the 3550–3250 cm^{-1} region that are relatively broad and are essentially a Gaussian type distribution. Enthalpies of hydrogen bond formation of copolymers in 2,4-TDI and *m*-XDI systems are listed in Table VII. In the copolymers, the interassociation enthalpy is higher than the intra-association enthalpy. PDMS urethane reacts with MMA by chemical bonding; hence, PDMS urethane will disperse easily in PMMA when the MMA content in copolymer is higher.
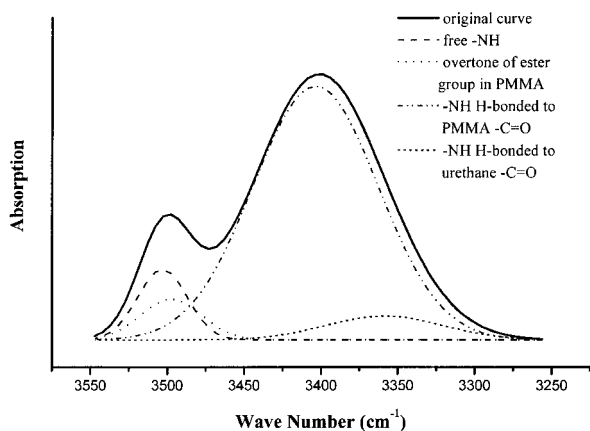
In the m-XDI system, the interassociation enthalpy (−2.44 kcal/mol) is greater than the intra-association enthalpy (−3.05 kcal/mol). The difference between interassociation enthalpy and intra-association enthalpy in the 2,4-TDI copolymer is higher than that in the *m*-XDI copolymer. The interassociation reaction in 2,4-TDI is more easily formed than that in *m*-XDI. However, the urethane group of PDMS segments were agglomerated; consequently, phase separation may occur in the *m*-XDI copolymer.

The ratio of the apparent integrated molar absorption coefficient of free, intra-association hydrogen bonding, and interassociation hydrogen bonding of the urethane group is 3:1:1 in the TBEU and XBEU systems. From Figures 12 and 13, the fraction of hydrogen bonding can be calculated by eq. 4. The results are listed in Table VIII.

$$f_{\text{PMMA}} = A_{\text{PMMA}}/[A_{\text{PMMA}} + A_{\text{ure}} + (A_{\text{free}}/3)] \qquad (4)$$

where f_{PMMA} is the fraction of interassociation hydrogen bonding, A_{PMMA} is the area of interassociation hydrogen-bonded urethane band, A_{ure} is the area of intra-association hydrogen-bonded urethane band, and A_{free} is the area of free urethane band.

Figure 12 Curve-fitting results of IR spectra of SiT22.5.

TABLE VII
Enthalpies of Hydrogen Bond Formation of Copolymers in *m*-XDI and 2,4-TDI Systems

Group	*m*-XDI system		TDI system	
	Peak (cm^{-1})	Enthalpy (kcal/mol)	Peak (cm^{-1})	Enthalpy (kcal/mol)
Overtone of carbonyl group	3497	—	3497	—
"H–free"—NH	3516	—	3503	—
—NH H-bonded to ester of PMMA	3443	−2.44	3403	−3.21
—NH H-bonded to urethane of grafted chain	3385	−3.05	3361	−3.58

TABLE VIII
Curve-Fitting Results of IR Spectra of Copolymers in 2,4-TDI and *m*-XDI Systems

Copolymer	"H-free"—NH	—NH H-bonded to PMMA —C=O	—NH H-bonded to urethane —C=O	f_{ure}[a]	f_{PMMA}[a]
SiT22.5	2.66	24.1	2.11	0.078	0.889
SiT15	0.70	9.99	0.74	0.067	0.911
SiT7.5	0.95	10.0	0.69	0.063	0.909
SiT3.75	0.31	4.84	0.22	0.043	0.937
SiX22.5	1.72	11.7	6.96	0.362	0.608
SiX15	1.31	8.11	3.86	0.311	0.654
SiX7.5	0.51	6.12	1.96	0.238	0.742
SiX3.75	0.44	3.40	0.84	0.191	0.775

[a] Molar fraction of urethane/PMMA or urethane/urethane hydrogen bonds.

The intra-association hydrogen bonding present indicated that the siloxane segments of different molecules aggregated, thereby causing phase separation easily. Curve-fitting results of IR spectra of copolymers in 2,4-TDI and *m*-XDI systems are listed in Table VIII. There is ~90% inter-association hydrogen bonding in the 2,4-TDI system, indicating the system is miscible. The intra-association hydrogen bonding in the *m*-XDI system is higher than that in the 2,4-TDI system. The fraction of hydrogen bonding agrees well with the enthalpy data. Therefore, aggregation and phase separation may occur in the siloxane-grafted chain in the *m*-XDI system.

Abrasion resistance of homopolymer PMMA and copolymers

The abrasion resistance of copolymer is better than that of homopolymer PMMA, as shown in Table IX. The weight loss and wear index of copolymer decreased with the increase of macromonomer content because of low surface energy and lower efficiency of PDMS for macromonomer. Therefore, PDMS present in the copolymer exhibited better abrasion resistance.

CONCLUSIONS

The crosslinking density data indicate that PDMS urethane–g–PMMA copolymers contain <2 wt % soluble

species. Therefore, the PDMS urethane–g–PMMA copolymers with low crosslinking density were synthesized in this study.

The tan δ curve of SiX22.5 shows that α relaxations of PMMA and PDMS segments occur at 131 and −110 °C, respectively, indicating PDMS urethane and PMMA segments in the *m*-XDI system are partially miscible. The tan δ curve of SiT22.5 shows that PDMS-urethane and PMMA segments are mixed well because the α relaxation of PMMA segments in SiT22.5 is present at 126°C, close to that of SiX22.5. The DMA results imply that the compatibility of the copolymer in the 2,4-TDI system is better than that in the *m*-XDI system. The T_gs of copolymers in the *m*-XDI system are independent of the macromonomer content, although the T_{gs} are lower than that of PMMA homopolymer. On the other hand, in the 2,4-TDI system, increasing macromonomer content will decrease the T_gs of PMMA segments of copolymers, indicating good miscibility.

Because the interassociation enthalpy is higher than the intra-association enthalpy in the macromonomers and copolymers, the interassociation hydrogen is the major hydrogen bonding in macromonomers and copolymers. The difference between interassociation enthalpy and intra-association enthalpy in the 2,4-TDI copolymer is higher than that in the *m*-XDI copolymer. The interassociation reaction in the 2,4-TDI system is more easily formed than that in the *m*-XDI system. The intra-association hydrogen bonding present indicated that the siloxane segments of different molecules aggregated, causing phase separation easily. There is ~90% interassociation hydrogen bonding in the 2,4-TDI system, indicating the system is miscible. The intra-association hydrogen bonding in the *m*-XDI system is higher than that in the 2,4-TDI system. The fraction of hydrogen bonding agrees well with the enthalpy data. Therefore, aggregation and phase separation may occur in the siloxane-grafted chain in the *m*-XDI system.

TABLE IX
Abrasion Resistance of Homopolymer PMMA and Copolymers

Polymer	Abrasion Weight loss (mg/500 cyclo)	Wear index (mg/cyclo)
PMMA	5.6	11.2×10^{-3}
SiX7.5	3.8	7.6×10^{-3}
SiX15	2.1	4.2×10^{-3}
SiT7.5	2.3	4.6×10^{-3}
SiT15	1.9	3.8×10^{-3}

References

1. Sperling, L.H.; Sarge III, H.D. J Appl Polym Sci 1972, 16, 3041.
2. Inoue, H.; Ueda, A.; Nagai, S. J Polym Sci: Part A 1988, 26, 1077.
3. Blahovici, T.F.; Brown, G.R. Polym Eng Sci 1987, 27, 1611.
4. Chujo, Y.; Murai, K.; Yamashita, Y. Makromol Chem 1985, 186, 1203.
5. Kawakami, Y.; Karasawa, H. Polym J 1985, 17, 1159.
6. Kawakami, Y.; Aswatha, R.; Murthy, N.; Yamashita, Y. Makromol Chem 1984, 185, 9.
7. Smith, S.D.; DeSimone, J.M.; Huang, H.; York, G.; Dwight, D.W.; Wilkes, G.L.; McGrath, J.E. Macromolecules 1992, 25, 2575.
8. Harvey III, T.B.; Scottsdale, A. U.S. Pat. 4,711,943 (1987).
9. Fowkes, F.M.; Tischler, D.O., et al. J Polym Sci: Polym Chem Ed 1984, 22, 547.
10. Kwei, T.K.; Pearce, E.M.; Ren, F.; Chen, J.P. J Polym Sci: Part B 1986, 24, 1597.
11. Hepburn, C. Polyurethane Elastomers, 2nd ed.; Elsevier: London, 1992; Chap. 3.
12. Ma, C.C.M.; Du, Y.C.; Wang, F.Y.; Wang, H.C.; Yang, J.C. J Appl Polym Sci 2002, 83, 1875.
13. Purcell, K. F.; Stikeleather, J.A.; Brunk, S.D. J Am Chem Soc 1969, 91, 4019.
14. Drago, R.S.; O'Bryan, N.; Vogel, G.C. J Am Chem Soc 1970, 92, 3924.
15. Fowkes, F.M.; Tischler, D.O. J Polym Sci: Polym Chem Ed 1984, 22, 547.
16. Kwei, T.K.; Pearce, E.M.; Ren, F.; Chen, J.P. J Polym Sci: Part B 1986, 24, 1597.
17. Paik Sung, C.S.; Smith, T.W. Macromolecules 1980, 13, 117.
18. Moskala, E.J.; Howe, S.E.; Painter, P.C.; Coleman, M.M. Macromolecules 1984, 17, 1671.
19. Coleman, M.M.; Xu, Y.; Painter, P.C. Macromolecules 1994, 27, 127.
20. Tanaka, T.; Yokoyama, T.; Yamaguchi, Y. J Polym Sci: Part A-1 1968, 6, 2137